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The mineralogy of the Grassy Creek and Saverton formations

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THE MINERALOGY
OF
THE GRASSY CREEK AND SAVERTON FORMATIONS

BY

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THESIS

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A B S T R A C T

A study of the mineralogy of the Grassy Creek and Saverton formations of Northeast Missouri was undertaken to determine whether a division is justified, as proposed by some stratigraphers, of these argillaceous beds into two formations. The formations were sampled systematically at surface exposures on the northeast limb of the Lincoln Arch in the vicinity of Hannibal and Louisiana, Missouri. The samples were investigated mineralogically in the laboratory. Previous studies showed that the fossils of the Grassy Creek and Saverton beds were virtually identical. The present study demonstrates that the Grassy Creek and Saverton beds are too near alike in mineral content and depositional environment to justify separation into two distinct formations. The diastem responsible for confounding stratigraphers into division of the beds into two formations was recognized as a relatively ephemeral, and in all probability local, feature. It is here proposed that the name Saverton for the upper beds be abandoned, and that the beds in their entirety be designated as the Grassy Creek formation.

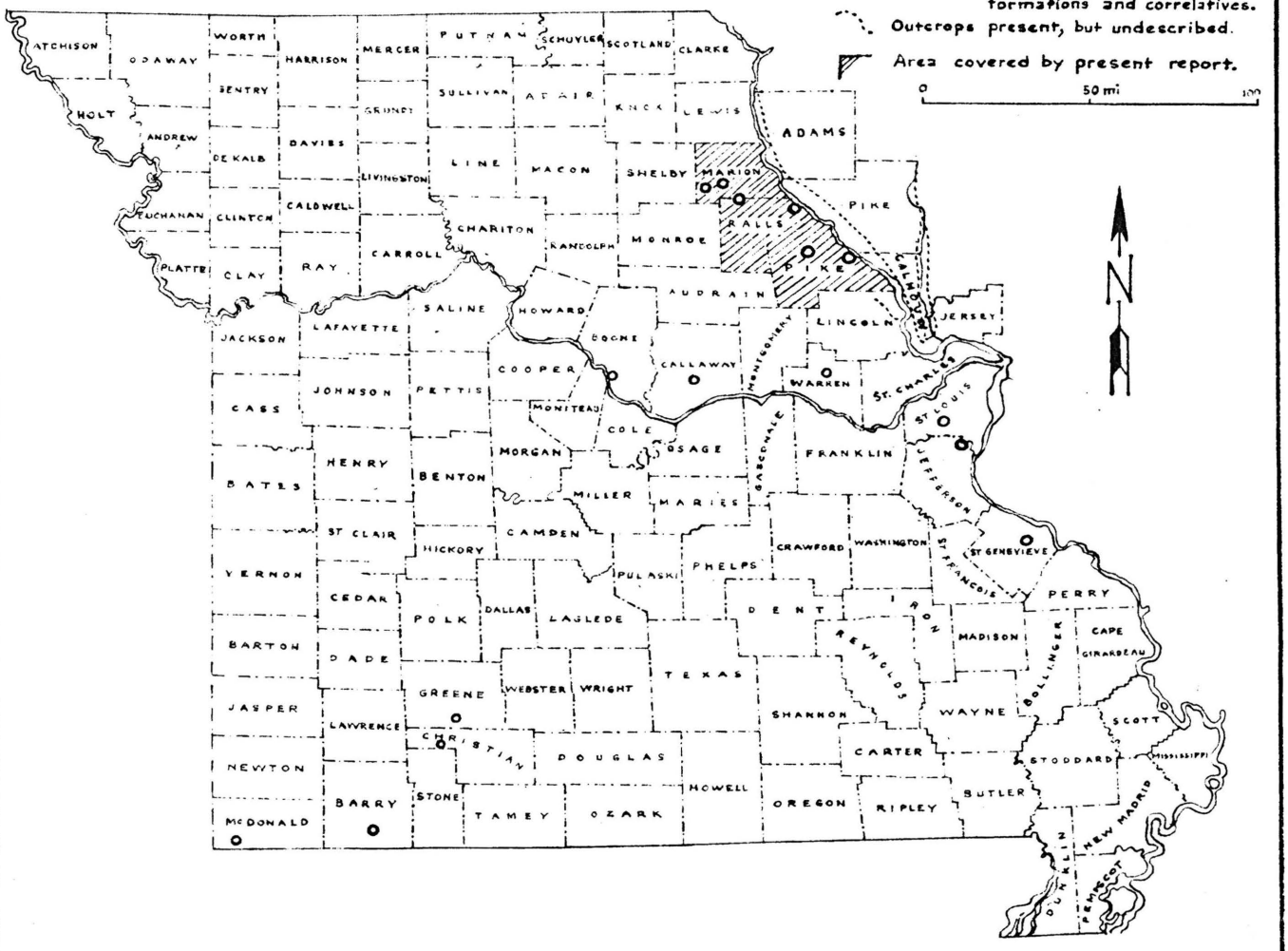
INTRODUCTION

In Marion, Ralls, and Pike Counties, Missouri, beds designated as the Grassy Creek formation, consisting almost entirely out of dark brown organic shale, are overlain by predominantly gray-green shales and siltstones which have been designated as the Saverton formation. Controversy has existed for some time regarding the designation of these upper beds as a separate formation. The existence in surface exposures of a sudden transition from dark brown, highly fissile shale to gray-green, non-fissile shale led Keyes to assign formational status to the upper beds. The fact that the beds contain virtually identical fossils and have approximately the same areal extent favors the earlier view that all of the beds belong to a single formation.

The writer was introduced to this problem by Dr. O. R. Grawe, and the work was carried out to assist Mr. W. R. Higgs, who is mapping these formations in the Silex quadrangle under the direction of Dr. A. C. Spreng. All of these men accompanied the writer into the field, introduced him to the stratigraphy, showed him where the formations are exposed, and suggested a sampling procedure to be followed in a study of the mineralogy of the shales.

The areas of outcrop of the Saverton, Grassy Creek and equivalent formations in Missouri are shown in Figure 1. Figure 2 shows the localities in Marion, Ralls, and

Pike Counties where the writer measured sections and obtained samples for mineralogic study.



APPROXIMATE DISTRIBUTION
OF
GRASSY CREEK, SAVERTON, AND CORRELATIVE FORMATIONS
IN
MISSOURI AND ADJACENT WESTERN ILLINOIS

Figure 1

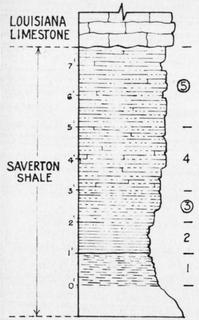
STRATIGRAPHY

ORIGIN OF NAMES

Until 1913 the shales which immediately underlie the Louisiana limestone in Marion, Ralls, and Pike Counties were designated by the formational name Grassy Creek. In 1913 Keyes (1913, pp. 160-164) gave the name Saverton to the gray-green shale immediately below the Louisiana limestone and restricted the term Grassy Creek to the dark brown fissle shale below the gray-green material. The contact between the two is sharp. This is due partly to the high development of fissility in the lower beds as compared to the more massive structure of the upper ones, and partly to the color contrast from dark brown below to gray-green above. Since 1913, some writers have followed Keyes, restricting the term Grassy Creek to the lower fissile dark brown shale, while others have continued the earlier usage, calling both the fissile dark brown shale and the overlying soft gray-green shale Grassy Creek. To avoid confusion in the review of the work of previous investigators, the present writer will designate the usage of the name Grassy Creek in the restricted sense by (s.s.) and the broader usage by (s.l.).

The name Grassy Creek (s.l.) was used first by Keyes (1897, pp. 55-58 . Later he (1922, pp. 307-310) referred to the formation as the Grassy shale. Udden (1899, p. 301)

named a stratigraphically equivalent shale in Muscatine County, Iowa, Sweetland Creek. According to Keyes (1940, pp. 146-148) this shale is probably a correlative of the Saverton formation. Harris (1947, p. 25) believed the Maple Mill formation of southeastern Iowa to be correlative with at least part of the Saverton and Grassy Creek formations. Ulrich (1904, p. 101) gave the name Noel to a correlative of the Grassy Creek formation (s.l.) in southwestern Missouri and adjacent Arkansas. In Jefferson County, Missouri, he used the term Sulphur Springs for a sequence of strata which now is known to include Grassy Creek shale (s.l.), Glen Park limestone, and Bushberg sandstone. Rowley (1908, p. 24) called the Grassy Creek (s.l.) Hamilton shale. Krey (1924, p. 33) referred to the formation as the Sweetland Creek, not recognizing the priority of the name Grassy Creek (s.l.). Weller (1935, pp. 191-192) misused the name Saverton to include not only the upper gray-green shale, but also the lower dark brown shale. Branson (1944, p. 159) did not recognize enough difference between the gray-green and the dark brown shales to warrant giving the former formational status and a separate name. Accepting its priority, he continued to use the name Grassy Creek (s.l.) for both formations. Branson (1944, p. 167) also pointed out that many authors refer to the Grassy Creek (s.l.) as Chattanooga shale.



5 Siltstone, slightly calcareous, massive-bedded, light gray. (2.5')

4 Siltstone, calcareous, massive-bedded, light gray. (2')

3 Siltstone, argillaceous, massive bedded, medium gray. (1')

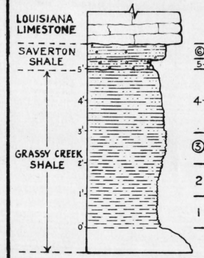
2 Shale, medium-bedded, dark gray. (1')

1 Clay shale, thin-bedded, blue-gray, weathers to rust-brown. Streaks of limonite. (1')

Concealed

SECTION VI

S.½ Sec. 7, T.5S., R.3W., 1 mi. N.W. of Saverton.



6 Siltstone, slightly argillaceous, light gray. Disseminated, coarse, round, frosted quartz grains. (0.5')

5 Clay, arenaceous, greenish-brown. Streaks of limonite. Abundant coarse, round, frosted quartz grains. (0.5')

4 Shale, slightly arenaceous, thin-bedded to fissile, gray-brown. Small lenses lighter-colored, more silty shale. (2')

3 Clay shale, slightly arenaceous, thin-bedded, gray-brown. (1')

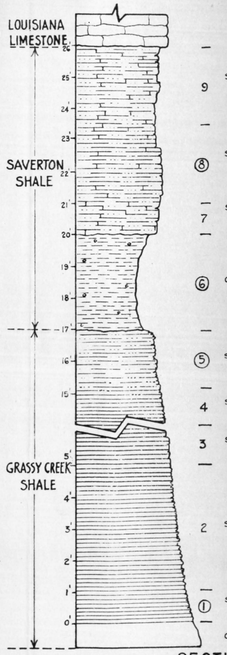
2 Clay shale, slightly arenaceous, thin-bedded, gray-brown. (1')

1 Clay shale, thin-bedded, light gray-green. (1')

Concealed.

SECTION VII

N.E.¼ T.56N., R6W., W. of bridge across South River, Hwy. 36



9 Siltstone, very calcareous, slightly argillaceous, thin-to-medium-bedded, light gray-green. (2.5')

8 Siltstone, calcareous & argillaceous, thin-to medium-bedded, medium gray-green. (2.5')

7 Siltstone, very calcareous, slightly argillaceous, thin-to medium-bedded, light gray-green. (1')

6 Clay, brownish olive-green. Disseminated, coarse, round, frosted quartz grains. (5')

5 Shale, arenaceous, thin-bedded, dark gray, weathers to light gray. (2')

4 Shale, thin-bedded, dark brown, weathers to gray. (5')

3 Shale, thin-bedded, dark brown, weathers to gray. (5')

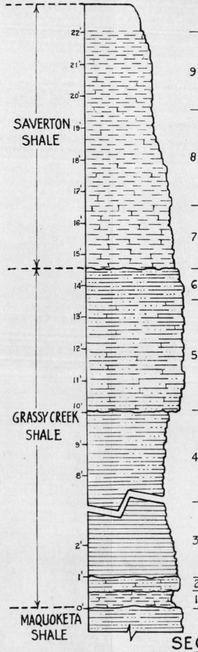
2 Shale, fissile, dark brown, weathers to purplish-brown. (4')

1 Shale, thin-bedded, dark brown, weathers to gray. (1')

Concealed.

SECTION V

S.E. ¼ Sec. 24, T.56N., R.4W., 2 mi. S.E. of Saverton on Ilasco Creek.



Concealed.

9 Clay shale, calcareous, thin-bedded, light blue-green. (2.5')

8 Clay shale, calcareous, thin-bedded, light olive-green. (3')

7 Clay shale, very calcareous, fissile, light green, weathers to green clay. (2')

6 Siltstone, argillaceous, thin-bedded, buff. Small lenses darker colored shale. (1')

5 Siltstone, calcareous, slightly argillaceous, thin-bedded, buff to brown. (3½')

4 Shale, arenaceous, thin-bedded, dark brown. More laminae of silt toward top of unit. (5')

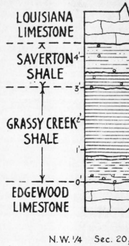
3 Shale, fissile-to thin-bedded, dark brown. (4')

2 Siltstone, calcareous, dark brown (0.4')

1 Clay shale, calcareous, greenish-brown. (0.5')

SECTION III

S.E. ¼ Sec. 19, T.54N. R.2W., on Grassy Creek.



8 Siltstone, calcareous, slightly argillaceous medium-bedded, buff. Disseminated, coarse, round, frosted quartz grains. (0.5')

7 Siltstone, slightly argillaceous, medium-bedded, light greenish-gray. Disseminated, coarse, round, frosted quartz grains. (0.4')

6 Shale, medium-bedded, gray-green. Streaks of limonite. Coarse, round, frosted quartz grains. (0.5')

5 Shale, thin-bedded, brown, weathers to dark greenish-gray. (0.1')

4 Shale, fissile, dark brown, weathers to purplish-brown. (2')

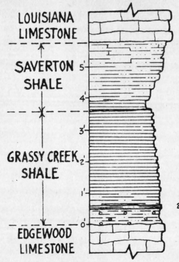
3 Sandstone, medium-grained, hard, white to brown. (0.1)

2 Clay, blue-green. Streaks of pyrite and limonite. (0.4')

1 Clay, arenaceous, greenish-brown. Streaks of limonite. Abundant, coarse, round, frosted quartz grains. (0.4')

SECTION I

N.W.¼ Sec. 20, T.54N., R.1W., S.E. part of Louisiana in Mississippi River Bluff.



6 Siltstone, slightly argillaceous, calcareous toward top, massive-bedded, medium gray. (0.9')

5 Shale, arenaceous, massive-bedded, light gray. (0.8')

4 Shale, blue-green. Disseminated, coarse, round frosted quartz grains. (0.5')

3 Shale, thin-bedded, dark brown, weathers to purplish-brown. (2.7')

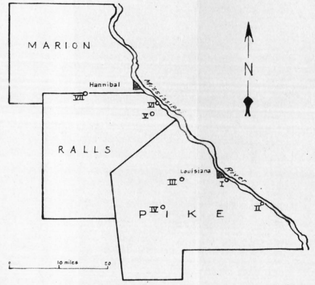
2 Shale, slightly arenaceous, dark brown, thick-bedded. (0.4')

1 Shale, arenaceous, blue-gray. (0.1')

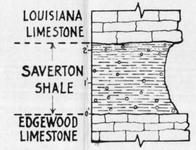
Clay shale, slightly arenaceous, yellow-green. Streaks of limonite. Abundant, coarse, round, frosted quartz grains. (0.5')

SECTION II

S.W.¼ Sec. 7, T.55N., R.1E., ½ mi. N.W. of Clarksville in Mississippi River Bluff.



KEY MAP SHOWING LOCATION OF SECTIONS



3 Clay shale, arenaceous, green-gray. Small glauconite fragments. Abundant coarse, round, frosted quartz grains. (0.2)

2 Clay shale, gray-blue. Abundant coarse, round, frosted quartz grains. (1')

1 Clay shale, blue-green, Abundant coarse, round, frosted quartz grains. (1')

SECTION IV

N.W.¼ Sec. 13 T.55N., R.3W., Magnesium Mining Co. quarry.

SECTIONS MEASURED ON OUTCROP OF GRASSY CREEK & SAVERTON FORMATIONS

MARION, RALLS, & PIKE COUNTIES
MISSOURI

LEGEND

- Limestone.
- Sandstone.
- Shale.
- Siltstone or arenaceous shale.
- Calcareous siltstone.
- Clay or clay shale.
- Arenaceous clay or Arenaceous clay shale.
- Calcareous clay or Calcareous clay shale.
- 3/5 Sample number & interval.
- (4) Sample analyzed.
- (2.5') Thickness interval.

Figure 2

LOCATION OF TYPE SECTIONS

Keyes (1897, pp. 55-58) first described the Grassy Creek formation (s.l.) from a section in N. W. ¼ Sec. 20, T. 54 N., R. 1 W. in the southeast part of the town of Louisiana, Pike County, Missouri. He also referred to the presence of the formation in N. E. ¼ Sec. 19, T. 54 N., R. 2 W. on Grassy Creek, 6 miles west of Louisiana. This section was later described by Rowley (1908, pp. 24-26). Weller (1935, pp. 191-192) pointed out that Rowley did not distinguish a lower, lighter gray shale from the overlying darker beds and that this lighter gray shale contains graptolites of Ordovician Maquoketa age. In the section at Louisiana, Grassy Creek beds (s.s.) rest on Silurian Edgewood limestone, a more easily recognized contact. The upper contact with the Saverton beds likewise is a sh p one in this locality. The section at Louisiana therefore is believed by some to be a more desirable type section for the Grassy Creek formation than the one on Grassy Creek. For descriptions of the sections at Loui iana and on Grassy Creek, the reader is referred to Sections I and III, Figure 2.

Keyes (1913, pp. 160-164) named the Saverton formation from exposures in the vicinity of Saverton, Ralls County, Missouri, about 7 miles southeast of the town of Hannibal, the best section being in S. E. ¼ Sec. 24, T. 56 N., R. 4 W. on Ilasco Creek. For description of the

section, the reader is referred to Section V, Figure 2. Williams (1943, pp. 4-5) stated that at its type locality the Saverton shale grades downward into the underlying Grassy Creek shale, but a careful examination of the section by the present writer revealed the contact.

LITHOLOGY

The greater portion of the Grassy Creek formation (s.s.) is thin-bedded to fissile shale, dark brown on a freshly broken surface and dark blue-gray on a weathered surface. The shale breaks up into very thin slabs, which cover the slopes below the outcrops. Abundant organic material gives the shale its brown color. Krey (1924, p. 63) stated that oil can be distilled from the shale. Rowley (1908, p. 26) pointed out the suitability of the shale for manufacturing Portland cement. Kurtz (1953, p. 19 and p. 81) mentioned that the shale possesses excellent bloating characteristics for the manufacture of light aggregate for concrete.

At Louisiana, the lower few inches of the Grassy Creek formation consist of a greenish-brown arenaceous clay shale with abundant, coarse, round, frosted sand-grains. This material is overlain by a few inches of blue-green clay shale, which contains abundant pyrite and is succeeded above by one inch of medium-grained, hard sandstone. At Clarksville and on Grassy Creek the

formation shows a similar succession of clay-like and sandy material at the base. According to Krey (1924, p. 62) the basal portion of the formation is sandy in Pike County, Illinois. Krey (1924, p. 33) also stated that the formation becomes more sandy toward the west and that at Brushy Creek, Ralls County, Missouri, it contains several well-defined beds of sandstone.

The Saverton formation grades from a soft grayish-green clay shale with streaks of coarse, frosted, sand-grains at the base through a greenish-gray argillaceous siltstone to a gray or buff-colored slightly argillaceous siltstone at the top. According to Moore (1928, p. 37) the formation locally contains thin beds of rather soft, bluish limestone; it may be represented also by soft, massive sandstone.

In all sections examined by the present writer, the contact between the Saverton and the underlying Grassy Creek (s.s.) formation is easily recognized by the sudden transition from dark brown, fissile, silty shale of the lower formation to the gray-green, more massive clay shale of the upper formation. The contact between the Saverton and the overlying Louisiana is a sharp one in most sections, being marked by a change from shale to limestone.

DISTRIBUTION AND THICKNESS

Branson (1944, p. 159) stated that outcrops of the Grassy Creek formation (s.l.) are found largely in Ralls, Marion, Pike, and Lincoln Counties. One outcrop is found in the Missouri River bluffs between Providence and Easley in Boone County, and was described by Unklesbay (1952, pp. 40-41). Another outcrop is found 2 miles east of Warrenton in Warren County. Equivalent outcrops occur in Ste. Genevieve County, in Jefferson County, and in St. Louis County at Castlewood on the Meramec River. (See Figure 1.) Krey (1924, pp. 23-24) measured 60 feet of Grassy Creek (s.l.) in Lincoln County and 100 to 125 feet in Pike and Ralls Counties. According to the same author, 150 to 200 feet of the beds can be found in Adams County, Illinois. Grohskopf et al. (1939, p. 15) assigned 85 feet of shale to the Grassy Creek (s.l.) in a well-section in Lewis County. Both Krey and Grohskopf pointed out that the thickness of the beds decreases to 25 feet a hundred miles west of the Mississippi River and that the beds have been identified in cuttings from wells as far north as the state line. According to Moore (1928, p. 34) the Grassy Creek formation (s.s.) is exposed at the surface in Pike and Calhoun Counties, Illinois, where it has a thickness of 20 feet. The beds thin and disappear southward. The Grassy Creek formation (s.s.) appears to thicken northeastward, the greatest increase in thickness being toward

the Illinois basin.

Due to lack of distinction between the Grassy Creek and the Saverton formations, little is known concerning the distribution of the latter. Moore (1928, pp. 37-38) stated that the Saverton beds occur in Marion, Ralls, and Pike Counties and may be present in Lincoln County, Missouri. He indicated thicknesses for the Saverton formation of 30 feet in Pike County and 50 to 100 feet in Ralls County. He also recorded Saverton beds in Pike and Calhoun Counties, Illinois. Moore (1935, p. 239) admitted in a later publication that he had erroneously included Maquoketa shale in one of his measurements of the Grassy Creek (s.s.). He believed the thickness of the latter probably does not exceed 20 feet. The distribution of the Saverton formation appears to be approximately the same as that of the Grassy Creek (s.s.), except that the Saverton extends farther to the south and probably farther north. Keyes (1940, p. 146), for example, stated that the Saverton is exposed at waterlevel in the Mississippi River at Burlington, Iowa. Harris (1947, pp. 22-25), on the other hand, mentioned the occurrence of the characteristic dark brown shale as well as the overlying gray-green shale in the basal Mississippian Maple Mill formation of southeastern Iowa. He considered the Maple Mill formation at least partly correlative with the Grassy Creek (s.s.) and Saverton formations of Missouri.

The present writer measured sections in Marion, Ralls, and Pike Counties, Missouri, and the maximum thicknesses found for the Grassy Creek (s.s.) and Saverton formations were 17 and 9 feet respectively as recorded in Sections I to VII, Figure 2. From such direct measurements he believes that the thicknesses reported previously by Krey, Moore, and Grohskopf should be regarded with some reservation.

RELATION TO OTHER FORMATIONS

Throughout the region of this study, an important unconformity exists at the base of the Grassy Creek formation. According to Branson (1944, p. 128) and Moore (1928, p. 34 and 1935, p. 239) the Grassy Creek formation and its correlatives rest on formations ranging from Lower Ordovician to Upper Devonian. The shales rest on Ordovician Plattin and Kimmswick limestones in Warren County, on Fernvale limestone in Jefferson County, and on Maquoketa shale in St. Louis, Ralls, and Marion Counties; on Silurian Edgewood and Sexton Creek limestones in Pike County; on Devonian Cooper, Mineola, and Callaway limestones in Boone County.

Throughout most of their extent, the southern correlatives of the Saverton formation are overlain unconformably by the Mississippian Bushberg sandstone. In Pike County, Saverton shale is overlain conformably by Louisiana

limestone. According to Branson (1944, p. 174) the Louisiana limestone grades into the shale in places. South of St. Louis, dark brown and green shales occur below the Bushberg sandstone. These shales, which are correlative with the Grassy Creek (s.l.), are intersected by a limestone referred to the Glen Park by Branson (1944, p. 174). Branson (1944, p. 161) stated that the Saverton formation is overlain unconformably by the Mississippian Hannibal shale in Lincoln and Ralls Counties. Moore (1928, p. 38) indicated that the Saverton beds are overlain either by the Louisiana limestone or by the Hannibal shale in Pike and Calhoun Counties, Illinois. Krey (1924, p. 34) found that in southern Calhoun and Jersey Counties, Illinois, the Grassy Creek (s.l.) is absent and that the Louisiana limestone overlies older Devonian formations.

AGE AND CORRELATIONS

The most common fossils in the Grassy Creek formation (s.l.) and its correlatives are fish-teeth, fish-bones, coprolites, and organic remains resembling spores. Invertebrate fossils are not very common, and Branson (1923, p. 6) stated that most of the invertebrates found in the Grassy Creek (s.l.) are of little value for correlation purposes. An exception, perhaps, is a distinctive ostracod mentioned by Moore (1928, p. 42), found near the top of the Saverton shale by R. S. Bassler. This

ostracod is characteristic of the Ridgetop shale of Tennessee, a formation which occurs immediately above the Chattanooga shale of that area. Moore (1928, pp. 40-42) brought out the fact that 25 of the 32 invertebrate species present in the Saverton formation occur also in the Louisiana limestone.

Rowley (1908, pp. 24-25) was the first to collect fish remains from the Grassy Creek. Branson and Mehl have done most of the work on the fish remains since then. Branson (1934, p. 172) identified fish remains from both the Saverton and the Grassy Creek formations, and concluded that these fossils furnish no evidence for differentiating between the two formations. Moore (1928, p. 42) stated that the fauna of the Saverton includes fishes considered diagnostic of the Devonian as well as some highly characteristic of the Mississippian. He inferred that Devonian sharks must have persisted into the Mississippian period.

Branson and Mehl (1934, p. 162) described a particularly large conodont assemblage from the Grassy Creek (s.l.). They (1934, p. 168) pointed out that these conodonts are typical of Upper Devonian formations elsewhere; to wit the Lower Huron of Ohio, the Portage of New York, the Chattanooga shale of Alabama, the Hardin sandstone of Tennessee, the Woodford of Oklahoma, and the Snyder Creek shale of central Missouri. They (p. 179) emphasized that the conodonts from the gray-green shale are

the same as those from the dark brown. Branson (1938, p. 179) remarked later that not only does the Grassy Creek formation (s.l.) contain Devonian conodont genera and no Mississippian genera, but that this is also true for the overlying Louisiana limestone. The Louisiana and the Grassy Creek (s.l.) even contain the same species, but the number of species is smaller in the Louisiana than in the Grassy Creek (s.l.). The Hannibal shale, which overlies the Louisiana, contains Mississippian genera while typically Devonian genera are absent. Thus, while the evidence derived from fish remains is inconclusive, the evidence from conodonts is strongly in favor of placing the Grassy Creek (s.l.) and Louisiana in the Upper Devonian and drawing the Devonian-Mississippian boundary below the Hannibal. Williams (1943, pp. 38-43), however, provisionally assigned the Louisiana limestone to the basal Mississippian or Kinderhookian on the basis of faunal correlation of brachiopods and pelecypods in the Louisiana limestone with those in the type section at Kinderhook.

According to Branson and Mehl (1934, p. 175) the Bushberg sandstone, which overlies the Grassy Creek in some areas, contains a typical Basal-Mississippian conodont fauna. In Boone and Callaway Counties, the Snyder Creek shale occurs below the Bushberg sandstone. This shale contains a conodont assemblage similar to that of the Grassy Creek formation (s.l.). The Snyder Creek

shale correlates with the dark brown Noel shale of Southwest Missouri, which bears the Grassy Creek conodont fauna in some places but carries the Bushberg fauna in others.

LABORATORY ANALYSIS

PREVIOUS WORK

The earliest record in this country of a mineralogical investigation of a shale as distinguished from that of a clay was published by Grim, Kerr, and Bray (1935, pp. 1909-1926). The authors disaggregated a laminated Cretaceous shale by treatment with ammonium acetate or dilute hydrochloric acid, studied the coarse fraction under the petrographic microscope, and investigated the fine fraction by means of X-ray diffraction photography and chemical analysis. Oriented aggregates of clay minerals were studied under the petrographic microscope. Minerals detected in the shale were quartz, orthoclase, sericite, kaolinite, beidellite, chlorite, white mica, sillimanite, epidote, rutile, zircon, tourmaline, and glauconite.

Fairbairn (1943, pp. 246-256) investigated slates and shales from Vermont by an entirely different technique. A thin section, cut perpendicular to the bedding, was mounted in a Laue camera perpendicular to the X-ray beam. The thin section was moved slowly to and fro during the exposure. Minerals identified in the diffraction pattern were quartz, muscovite-illite, kaolinite, and chlorite.

Bates (1947, pp. 625-636), in an investigation of

slate from northeastern Pennsylvania, ground the slate to a powder. Pyrite and carbonaceous matter were removed by flotation. The rest of the material was dispersed with sodium lignin sulphonate and fractionated. The coarse fraction was studied under the petrographic microscope, and the fine fraction was further separated into several sizes, which were studied by means of a Norelco X-ray spectrometer, the petrographic microscope (oriented clay mineral aggregates), differential thermal analysis, and electron micrographs. This work was supplemented by firing tests and X-ray-diffraction photographs. Bates identified quartz, feldspar, calcite, dolomite, illite, pyrite, rutile, graphite, and carbonaceous material in the slate, in addition to small amounts of chlorite (penninite) and sericite.

Gude (1950, pp. 1699-1718) sampled a section across the Upper Cretaceous Laramie formation and identified the prominent minerals in over a hundred samples. General Electric X-ray-diffraction equipment was employed, and the sample was prepared by rolling a thin rod out of powdered raw shale and Duco cement. Quartz, calcite, illite, kaolinite, montmorillonite, and limonite were identified by comparison with standard diffraction patterns of these minerals. Estimates were made for each sample of the relative amounts of the components on the basis of intensities of reflections. Dye tests for clay minerals in powdered raw shale gave indifferent results.

Keller and Ting (1950, pp. 123-132) investigated a single sample of the Pennsylvanian Perry Farm shale. They dispersed the powdered shale with acetic acid and separated it in several sizes. Coarse sizes were separated into heavy and light fractions with tetrabromoethane, aided by centrifugation. Each of these coarse fractions was examined under the petrographic microscope. The fine fractions were investigated with the aid of differential thermal analysis, X-ray powder diffraction patterns, electron micrographs, and infra-red absorption spectrograms. The shale was studied in thin section, and minor elements were determined by emission spectrography. Minerals detected were quartz, illite, orthoclase, microcline, plagioclase, carbonate (almost entirely calcite), kaolinite, possibly montmorillonite, chlorite, muscovite, sericite, biotite, pyrite, iron oxides, leucoxene, rutile, sphene, zircon, and tourmaline.

Keller (1953a, pp. 3-9) studied a number of shales and clays in an effort to determine the origin of the green color of argillaceous rocks. He made use of differential thermal analysis and a Norelco X-ray spectrometer.

Keller (1953b, pp. 93-105) also proposed a new subdivision of the Cretaceous Morrison formation on the basis of his study of clay minerals in the type section. Samples were ground to a powder and disaggregated in water. The fraction with particles below 2 microns in

diameter was analyzed with differential thermal apparatus and a Phillips X-ray spectrometer.

At the time of this writing, Bates (1953, p. 1529) is engaged in a mineralogical study of the Chattanooga shale, designed to be quantitative as well as qualitative. This investigation employs light and electron microscopy, X-ray diffraction, differential thermal analysis, thin section study, and radio-activity tests.

PRELIMINARY INVESTIGATION

Dispersion Tests

Of the various samples collected from the Grassy Creek and Saverton formations, two were selected, representative respectively of the most common lithologic facies of each. One sample consisted of a dark brown fissile shale, the other consisted of a light gray, massive, slightly calcareous siltstone. The samples were ground in an iron mortar and sieved through a 35 mesh screen. The sieved materials each were split into 6 portions of 20 grams to which were added respectively the following: 200 cc. water, 200 cc. water plus 5 grams sodium pyrophosphate, 200 cc. water plus 5 grams soda, 200 cc. water plus 10 cc. concentrated hydrochloric acid, 200 cc. water plus 30 cc. concentrated sodium hydroxide solution, and 200 cc. water plus 30 cc. of 30% hydrogen peroxide sol-

ution. The suspensions were left to stand for one day. As very little dispersion appeared to have occurred at the end of that time, the suspensions were heated and kept at a temperature close to boiling for two days. Since the suspension had not become dispersed at the end of this time, the particles were rubbed vigorously with a large rubber "policeman", after which a drop of each suspension was placed on a slide and examined under the petrographic microscope. Dispersion of the siltstone was considerably better than that of the shale, but it could not be considered satisfactory for either material. It was obvious, however, that treatment with hydrogen peroxide offered the greatest promise of success.

One hundred grams of the shale and the siltstone each were broken up in the iron mortar, after which the materials were ground as fine as possible in a 4 inch agate mortar. The fine powder was transferred to large beakers, and 100 cc. water was added to each. From then on, 30% hydrogen peroxide was added intermittently in small volumes, enough to maintain a constant stream of bubbles rising to the surface of the liquid. After continuing this process for about 2 days, the suspension of finest material was poured into another beaker. The coarser material was transferred in small portions to the agate mortar, where each portion was ground thoroughly before being transferred back to the original suspension. Treatment with hydrogen peroxide was now resumed for

2 more days, after which the technique of wet-grinding material that rapidly settled out of suspension was repeated. Hydrogen peroxide was added again, and the suspensions were left to stand. After a week, a drop of each was examined under the petrographic microscope. At least 90% of the material in each suspension proved to be completely dispersed.

Excess hydrogen peroxide was boiled off, and ammonium hydroxide was added to the suspensions to keep the clay-mineral particles from flocculating. The suspensions were settled in order to obtain fine suspensions containing only particles smaller than 2 microns in diameter. These fine suspensions were passed through a Sharples Super-Centrifuge to obtain super-fine suspensions containing only particles smaller than 0.3 micron in diameter. The fine and super-fine suspensions were evaporated, and the dried material was stored.

X-ray Diffraction

X-ray diffraction was initiated on three types of powdered materials: the finely-ground raw shale, the material of size-grade below 2 microns, and the material of size-grade below 0.3 micron. Subsequently, diffraction spectrograms were obtained of an oriented shale fragment and of an oriented aggregate of clay minerals.

Powder patterns - Debye-Scherer technique:

An attempt was made to obtain diffraction patterns on a General Electric XRD-type 1 X-ray unit, using an iron-target tube, the powder-wedge method of mounting the sample, and an exposure of 3 hours.

Examination of the diffraction patterns revealed that material smaller then 0.3 micron did not show any more clearly defined lines for the clay minerals than did the powdered raw shale. Of particular disappointment was the fact that no well-defined lines could be obtained at all in the 7 to 18Å range, i.e. the range where the clay minerals show basal-plane reflections. In an effort to remedy this condition, the films were exposed for 6 instead of for 3 hours, but no material improvement resulted.

Powder patterns - Phillips spectrometer:

Diffraction spectrograms were obtained on a North American-Phillips Recording X-Ray Spectrometer. The same three types of powdered material were tested, using a copper-target tube with and without a nickel filter, and an iron-target tube with and without a manganese filter. The samples were rotated over 45 degrees in 45 minutes, a recording pen recording the presence and also the intensity of each reflection.

The diffraction spectrograms for the finer size-

grades showed significantly better reflections for the clay minerals than did the raw-shale sample. The basal-plane reflections of the clay minerals could be recognized clearly. Several of the other high-Ångstrom reflections of the cla minerals could be distinguish d clearly from the reflections of quartz. Reflections were stronger with an iron-target tube than with a copper-target tube. Optimum reflections were obtained without filters. A further advantage of an iron target over a copper target is that reflections are less crowded together and can be differentiated more easily. Absence of a filter has the disadvantage of giving reflections for the β wavelength of the target as well as the α wavelength, but the β reflections are so much weaker than the α reflections that only the stronger α reflections are accompanied by β reflections. A simple diagram was constructed on a sheet of paper which gave the position of every β reflection relat've to α reflections spaced at regular intervals. Laying this diagram alongside the diffraction spectrogram enables one to recognize all β reflections immediately.

Shale-fragment pattern - Phillips spectrometer:

A diffraction pattern was procured from a fragment of raw shale. This fragment was mounted in the X-ray beam in such a fashion that the bedding plane was oriented like the surface of the packed powder in the previous

samples. The diffraction spectrogram was compared with one obtained from powdered raw shale. It was hoped that the clay minerals, being in preferred orientation, would give enhanced reflections, particularly basal reflections. Surprisingly, it was the reflections of quartz which were enhanced and not those of the clay minerals. The shale apparently consists of minute laminae, containing quartz and clay minerals in varying percentages; the X-ray beam happened to hit a lamina containing predominantly quartz.

Oriented aggregate pattern - Phillips spectrometer:

An oriented aggregate of clay minerals was obtained by the following procedure: The well-dispersed suspension was stirred and left to stand for approximately 36 hours. At the end of that period a glass slide was suspended in horizontal position at a depth of 6 inches below the surface of the liquid. Calculations based on Stokes's law indicated that material settling on the slide from the suspension would be smaller than 1 micron in diameter. The slide was left in the suspension for 2 days, after which it was pulled up carefully and allowed to dry. It was found that a superior oriented aggregate could be obtained by siphoning off the suspension until its surface was only $\frac{1}{2}$" above the slide and allowing evaporation slowly to lower the fluid level and dry the slide.

The diffraction spectrogram of the oriented material on the slide showed very strong clay-mineral reflections.

Basal-plane reflections had been enhanced strongly, but other reflections were only slightly stronger than in the diffraction pattern of raw shale. Reflections of quartz were still present but of minor significance. The clay-mineral flakes in settling out of suspension evidently oriented basal planes parallel to the glass slide while other crystallographic directions remained in random orientation.

Petrographic Work

Preparation of samples:

The two suspensions of dispersed material from which fine and super-fine particles had been removed were evaporated, and the residues were rubbed to a fine powder. Examination of these materials under the petrographic microscope revealed the difficulty of identifying minerals in a mixture of particles of varying sizes, particularly in the presence of a large number of lumps and flakes of clay minerals. It was deemed expedient to remove all material smaller than 10 microns in diameter before attempting identification, for no reliable mineral identification can be made with the petrographic microscope of smaller material.

Particles smaller than 10 microns in diameter were removed by long-continued elutriation under intermittent addition of small volumes of ammonium hydroxide to keep

the clay minerals deflocculated. The residues were dried and examined under the petrographic microscope. The clay-minerals had disappeared completely, leaving material consisting almost entirely of quartz.

Heavy mineral separation - by gravity:

The specific gravity of tetrabromoethane was adjusted to 2.9 by adding benzene until the liquid would just barely float a small crystal of dolomite.

The residues from which all material smaller than 10 microns in diameter had been removed were poured into tetrabromoethane in separating funnels. Particles exhibited considerable tendency to adhere one to another. Frequent stirring was employed to overcome this disadvantage. After one day, the heavy mineral concentrate at the bottom of the funnel was drawn off on filterpaper. Although nearly 50 grams of residue were poured into the heavy liquid, only a very few grains of heavy minerals were obtained. This "concentrate", futhermore, was contaminated heavily with quartz. Mere gravity separation did not suffice to secure clean separation between light and heavy minerals.

Heavy mineral separation - by centrifuge:

About 40 cc. of tetrabromoethane was poured in pear-shaped centrifuge-tubes with approximately 25 grams of residue. The tubes were shaken thoroughly, after which

they were whirled in a centrifuge for 20 minutes. At the end of this time interval, light minerals had collected at the top of the liquid, while heavy minerals had collected in the narrow tube at the base of the pear-shaped tubes. The light mineral fractions were discarded. Examination of the heavy mineral fraction under the petrographic microscope revealed that a clean separation of light and heavy minerals had been secured.

ADOPTED ANALYTICAL PROCEDURE

As a result of the preliminary investigation, the following analytical procedure was adopted as being appropriate to analysis of samples of the Grassy Creek and Saverton formations:

1. Seventy grams of shale were crushed and ground as fine as possible.
2. About 5 grams of the powder was stored for use in procurement of an X-ray-diffraction spectrogram with the Phillips spectrometer.
3. About 40 grams of the powder was disaggregated completely by alternate addition of 30% hydrogen peroxide solution and wet-grinding of material that settled rapidly out of suspension.
4. Excess hydrogen peroxide was boiled off and ammonium hydroxide was added, after which the suspension was blunged (turned end over end in a closed container)

for 12 hours.

5. The suspension was elutriated to yield a fraction with particles larger than 10 microns.

6. The material larger than 10 microns was dried, and a small portion of it was stored for microscopic examination. The rest was poured into a centrifuge tube which contained tetrabromoethane ($C_2 H_2 Br_4$) with a sp. gr. of 2.9.

7. The tube was whirled in a centrifuge. The heavy mineral fraction was collected from the bottom of the flask and stored for microscopic examination.

8. Water and a small amount of ammonium hydroxide were added to the remaining 25 grams of the finely ground shale. Material that settled rapidly out of suspension was removed, ground once more, and added to the suspension again. The suspension was stirred thoroughly and left to stand for 36 hours.

9. A glass slide was hung horizontally in the suspension at a depth of 6 inches below the surface of the liquid, so that clay could settle on the slide and produce an oriented aggregate.

10. After 2 days, the suspension was siphoned off until the surface of the liquid was only $\frac{1}{4}$" above the slide. Evaporation was allowed to lower the fluid level slowly below the slide.

11. The slide was used to obtain a diffraction spectrogram with the Phillips spectrometer.

SELECTION OF SAMPLES

Seven sections containing Grassy Creek and Saverton shale were examined, and 47 samples of the formations were collected. The purpose of laboratory analysis was to determine the mineralogy of the beds. More specifically, it was desired to determine whether the Grassy Creek and Saverton formations possessed a significant difference in mineral content. Accordingly, selection of samples for laboratory analysis from samples collected in the field was based on a compromise between the following criteria: 1. Samples should represent ypical and widespread lithologic facies. 2. Some samples should be selected on both sides of and adjacent to the Grassy Creek-Saverton contact. 3. Other samples in the same section should be selected at the greatest possible vertical distance from each other. 4. Samples should come from sections as far apart geographically as possible. The twelve samples selected for analysis are indicated by circled sample numbers in Figure 2.

RESULTS OF ANALYSIS

X-ray Diffraction Work

Standard Samples:

Spectrograms were made of nearly pure quartz, illite, kaolinite, montmorillonite, and chlorite. The spectrograms were used in identification of reflections of the shale.

The quartz spectrogram was obtained from a sample of tripoli from Seneca, Missouri. Reflections were checked against X-ray data for quartz compiled by Nagelschmidt (1934, pp. 120-145).

The illite spectrogram was obtained from A. P. I. Clay Mineral Standard H-?5. This standard is described by Kerr, Main, et al. (1950, p. 44). Reflections were checked against X-ray data for illite compiled by Kerr, Hamilton, et al. (1950, p. 28).

The kaolinite spectrogram was obtained from A. P. I. Clay Mineral Standard H-4. This standard is described by Kerr, Main, et al. (1950, pp. 19-21). X-ray data for kaolinite were procured from Grim (1953, p. 88).

The montmorillonite spectrogram was obtained from A. P. I. Clay Mineral Standard H-32. This standard is described by Kerr, Main, et al. (1950, pp. 39-40). X-ray data for montmorillonite were procured from Grim (1953, p. 92).

The chlorite spectrogram was obtained from a sample of prochlorite from Charlemont, Massachusetts. X-ray data were procured from Grim (1953, p. 98).

No spectrograms were made of muscovite, calcite, dolomite, or pyrite. X-ray data of these minerals were procured from Grim (1953, p. 94), Nagelschmidt (1934, p. 87), Mehmel (1939, pp. 92-118), and Ewald and Hermann (1931, p. 153).

After some experience, relative amounts of minerals could be estimated roughly by comparing intensities of reflections. The oriented clay mineral aggregates provided a check on the estimates of relative amounts of one clay mineral as compared to others.

Shale Samples:

The discussion which follows presents briefly for each mineral the evidence on which identification by X-ray diffraction was based as well as data relative to abundance and most common occurrence.

Quartz:

Quartz was identified in every spectrogram by a large number of reflections. Only reflections with an intensity of 6 or more for the α wavelength of iron gave recognizable reflections for the β wavelength. Examination of Table I indicates that quartz is either "abundant" or "very abundant" and that the Saverton formation contains more quartz than the Grassy Creek formation.

TABLE I
MINERALS IDENTIFIED IN THE GRASSY CREEK AND SAVERTON FORMATIONS OF MARION, RALLS, AND PIKE COUNTIES, MISSOURI

SECTION NUMBER	SAMPLE NUMBER	FORMATION (base, middle, top)	LITHOLOGIC DESCRIPTION	THICKNESS BED SAMPLED	MINERALS																	
					Major Components[1]								Minor Components[2]									
					Quartz[8]	Orthoclase[11]	Microcline[11]	Plagioclase[11]	Calcite[11]	Dolomite[10]	Illite[8]	Kaolinite[8]	Chlorite[9]	Muscovite[9]	Pyrite[9]	Goethite[9]	Leucoxene[9]	Rutile[9]	Zircon[9]	Phosphate[9]	Tourmaline[9]
I[3]	8	Saverton top	Siltstone, calcareous, slightly argillaceous, medium-bedded, buff. Disseminated, coarse, round, frosted quartz grains.	0.5'	Va				Ma	A	M	R	Ma	R		A	A	Ma	Vr	R	C
I	6	Saverton base	Shale, medium-bedded, gray-green. Streaks of limonite. Coarse, round, frosted quartz grains.	0.5'	Va	R				C	Va	M	A	C		A	A	Ma	A	Ma	M
I	4	Grassy Creek middle-top	Shale, fissile, dark brown, weathers to purplish-brown.	2'	A	M		R		M	Va	M	A	M	C	C	Va	Ma	M	C	R
I	2	Grassy Creek base	Clay, blue-green. Streaks of limonite and pyrite.	0.4'	A	C	Vr				Ma	Ma	Vr	Vr	Va				R	M	C
V[4]	8	Saverton middle	Siltstone, calcareous and argillaceous, thin- to medium-bedded, medium gray-green.	2.5'	A	M				A	M	R	M	C	C	C	Va	Va	C		R
V	6	Saverton base	Clay, brownish olive-green. Disseminated, coarse, round, frosted quartz grains.	3'	A	M			R[7]		A	M	C	M		A	A	R	Ma	R	R
V	5	Grassy Creek top	Shale, arenaceous, thin-bedded, dark gray, weathers to light gray.	2'	A	M			A[7]		A	C	Va	Ma	R	Ma	Ma	Va	R	M	A
V	1	Grassy Creek base-middle	Shale, thin-bedded, dark brown, weathers to gray.	1'	A				A[7]		A	M	A	A	A	A	R	R	Ma	R	A
VI[5]	5	Saverton top	Siltstone, slightly calcareous, massive-bedded, light gray.	2.5'	Va	M				Ma	C	Vr	R		Vr	R	C	A	A		Va
VI	3	Saverton middle	Siltstone, argillaceous, massive-bedded, medium gray.	1'	Va	R				Va	M	R	R	R	Vr	Va	C	C	M	R	C
VII[6]	6	Saverton middle	Siltstone, slightly argillaceous, medium-bedded, light gray. Disseminated, coarse, round, frosted quartz grains.	0.5'	Va	C				C	A	Vr	Ma		Va	C	A	M	C	M	R
VII	3	Grassy Creek middle	Clay shale, slightlyarenaceous, thin-bedded, gray-brown.	1'	A					A	Va	A	C	R	A	Ma	A	M	C	M	C

1) Each component comprises at least 5% of the sample. Very rare - very abundant 5 to 35%.

2) Each component comprises less than 5% of the sample. Very rare - very abundant 0.0 to 5%.

3) N.W.¼ SEC. 20, T.54 N., R.1 W., S.E. part of Louisiana in Mississippi River bluff.

4) S.E.¼ Sec. 24, T.56 N., R. 4 W., 2 mi. S.E. of Saverton on Ilasco Creek.

5) S.½ Sec. 7, T.5 S., R.3 W., 1 mi. N.W. of Saverton.

6) N.E.¼ T.56 N., R.6 W., W. of bridge across South River, Hwy. 36.

7) Calcite precipitated by treatment with hydrogen peroxide.

8) Relative abundance determined in X-ray spectrogram.

9) Relative abundance determined in heavy mineral concentrate.

10) Relative abundance determined in heavy and light mineral concentrates

11) Relative abundance determined in light mineral concentrate.

ESTIMATE OF RELATIVE ABUNDANCE

Symbol	Significance	Major Components	Minor Components
Va	Very abundant	35%	5%
A	Abundant	↓	↓
Ma	Moderately abundant		
C	Common		
M	Minor		
R	Rare		
Vr	Very rare	5%	0.0%

Illite:

Reflections used most frequently for the identification of illite were the basal reflections at 10.4 Å and at 4.97 Å and the (202) reflection at 2.59 Å. The high-value interplanar spacings are too high as compared with values given by others due to an instrumental error, which has been recorded here without correction. The basal (002) reflection was quite broad because the β reflection was immediately adjacent to the α reflection. All raw-shale spectrograms indicated the presence of illite. Illite was confirmed by strongly enhanced basal reflections in the oriented clay-mineral aggregates. Table I indicates that the relative amount of illite ranges from "minor" to "very abundant". The Grassy Creek shale contains more illite than the Saverton shale, the greatest quantity being present in the dark brown shale, and the least in the clay at the base of the Grassy Creek. The Saverton shale contains more illite in the argillaceous facies at the base than in the siltstone facies near the top.

Muscovite:

All reflections of muscovite coincide with or are at least partly overlapped by reflections of quartz, illite, or kaolinite. The 3.20 and 2.86 Å reflections are moderately strong for muscovite. Illite, however, gives only weak reflections at both 3.21 and 2.88 Å. The presence of moderately strong reflections at both

3.20 and 2.86 Å therefore was accepted as presumptive evidence of the presence of muscovite. The correctness of this reasoning was confirmed by the identification of the mineral under the petrographic microscope. Muscovite was identified in 8 out of 12 spectrograms. The spectrogram which showed not only the 3.20 and 2.86 Å reflections but also the 3.89, 2.78, 1.99, and 1.50 Å reflections of muscovite corresponded to the sample which showed the greatest amount of muscovite under the microscope. Data pertaining to the abundance of muscovite are based on microscopic work. For that reason, the occurrence of this mineral is discussed again in the section on petrography.

Kaolinite:

Reflections used to identify kaolinite were the basal reflections with apparent interplanar spacings of 7.2 Å, 3.57 Å, and 2.36 Å. Except the 7.2 Å reflection in the oriented clay mineral aggregates, none of the reflections was strong enough to be accompanied by a β reflection. Kaolinite was found in all samples. As Table I indicates, the relative quantity of kaolinite, ranging as it does from "rare" to "abundant", is subject to greater variation than that of illite. More significantly, there is a gradual decrease in kaolinite from the base of the section toward the top. Kaolinite is most abundant in the clay at the base of the Grassy Creek. The dark brown Grassy Creek shale contains only a minor

amount, as does the base of the Saverton. The siltstone-facies of the Saverton formation contains even less kaolinite.

Montmorillonite:

The spectrogram of the standard sample gave predominantly ill-defined reflections, with the exception of a good basal reflection at 15 Å. Treatment of the standard sample with ethylene glycol caused the basal reflection to shift to 18 Å.

Several of the raw-shale spectrograms showed a very indistinct reflection of about 15 Å. Treatment with ethylene glycol failed to shift this reflection. Some of the oriented clay mineral aggregates showed a pronounced reflection between 14 and 15 Å. Since treatment with ethylene glycol did not shift this reflection, montmorillonite is considered to be absent in the shales.

Chlorite:

Six raw-shale spectrogrmas showed reflections corresponding to the basal reflection at 14 Å of the standard sample of chlorite. Only one of these samples showed other chlorite reflections - namely, 3.55, 2.02, 1.97, 1.56, and 1.39 Å. The oriented clay mineral aggregates persistently showed a reflection at about 14 Å. These reflections at 14 Å could not be shifted by treatment with ethylene glycol. Unfortunately, the oriented aggregates were not rotated over a sufficiently large angle to obtain other chlorite reflections. The raw-shale

spectrogram which showed several chlorite reflections corresponded to the sample which showed the greatest amount of chlorite under the microscope. Data pertaining to the abundance of chlorite were based on microscopic work. The occurrence of this mineral therefore will be discussed further in the section on petrographic work.

Calcite:

Only one of the twelve raw-shale spectrograms exhibited the 2.28, 2.10, and 1.87 Å reflections of calcite. This suggests the absence of calcite in the other eleven samples. However, after the samples were treated with hydrogen peroxide, the petrographic microscope showed a considerable quantity of fine calcite needles in several samples. The absence of calcite lines in the spectrograms of the raw shale and the abundant presence of small calcite prisms in the sample after treatment with hydrogen peroxide indicates that calcite was newly formed by this treatment. Evidently, these prisms did not originate by solution of calcite by carbon dioxide (formed by reaction of hydrogen peroxide on organic matter) and subsequent reprecipitation. Rather, the calcite needles must have formed by combination of Ca^{++} ions removed from a clay mineral and $CO_3^{=}$ ions formed by oxidation of organic matter.

The fact that calcite was found in only one of the samples selected for analysis would be of little significance if, as indicated by Figure 2, material of similar lithology did not occur widely in the upper part of the

Saverton shale. (See Table I) Conceivably, the presence of calcite in this part of the Saverton shale foreshadowed conditions which gave rise later to deposition of the overlying Louisiana limestone.

Dolomite:

Reflections at 2.85, 2.65, and 2.18 Å signified the presence of dolomite in several samples. Dolomite was identified under the petrographic microscope in most samples. The occurrence of this mineral will be discussed in the section on petrographic work.

Pyrite:

Only one raw sample gave strong reflections at 2.69 and 1.63 Å. Pyrite euhedra were observed under the hand lens in this sample. Since pyrite was identified under the petrographic microscope in the majority of samples, the occurrence of this mineral will be discussed further in the section on petrographic work.

Petrographic Work

The following descriptions of minerals identified under the petrographic microscope are based upon the fraction of the shales larger than 10 microns and also on the heavy mineral concentrate derived from this fraction. Only those characteristics are noted which can be considered unusual or of special significance. It should be pointed out that the dispersion technique fractured the

larger grains, making identification of authigenic overgrowths and other features present in undamaged grains difficult.

Orthoclase:

Orthoclase occurs both as well-rounded and as euhedral, translucent, pale pink to gray grains. Most grains had a weathered aspect, being clouded by fine, slightly opaque material. Milner (1940, p. 322 stated that this material is secondary mica or kaolinite. The cloudy material included some iron oxide, for it was brown in reflected light. Translucent grains frequently exhibited rows of inclusions parallel to Z. The weathered aspect of the mineral indicates that it was not authigenic in the shale. The common occurrence of euhedral grains, however, points toward a previous authigenic origin. Krumbein and Pettijohn (1938, p. 442) pointed out that authigenic orthoclase is known from dolomite and limestone.

Microcline:

A single grain of microcline was detected in the blue-green clay at the base of the Grassy Creek. No significance can be attached to such a rare occurrence.

Plagioclase:

Several grains of plagioclase were found in one section of the dark brown shale facies of the Grassy Creek. Surprisingly, the mineral could not be detected in other sections of dark brown shale. The rounded grains were clouded with secondary mica or kaolinite.

Dolomite:

Dolomite occurred in several samples, always in roughly rhombohedral grains which were considerably larger than the average grain size of other minerals. The grains exhibited many spots of dark opaque material, probably iron and manganese oxide. Dolomite occurred locally and in minor amount in the dark brown shale facies of the Grassy Creek and was abundant in the clay-shale facies. Dolomite was present also throughout the silty facies of the Saverton formation. Toward the top of the Saverton shale, dolomite equaled quartz in abundance.

The large amount of dolomite in the Saverton shale seems to preclude authigenic origin. That the mineral entered the sediment by chemical precipitation during clastic deposition of the other minerals is possible. The marked association of dolomite with abundant and coarser-grained quartz and its relative absence from more argillaceous and finer-grained material points strongly in the direction of clastic origin. The large grain size might be due to recrystallization.

Near the top of the Saverton shale calcite is present as well as dolomite. It is believed that clastic deposition, predominantly of quartz and dolomite, gave way gradually to chemical deposition of limestone, culminating eventually in the deposition of the lithographic Louisiana limestone.

Chlorite:

Chlorite was present in all samples and exhibited a wide range of relative abundance. The mineral occurred in small round micaceous flakes, the color of which varied from pale green to medium blue-green. The small 2V could be determined only with great difficulty due to the small size of the flakes and the very low birefringence. Thicker flakes showed aggregate polarization. Which member of the chlorite family was represented was not determined. Krumbein and Pettijohn (1938, p. 425) listed chlorite as a product of low-grade anamorphism of clays and shales. Indeed, to assume that the mineral is detrital would pose the considerable problem of finding a source area of metamorphic rocks, the only rocktype besides shale itself that could supply chlorite in sufficient abundance. Chlorite was most abundant in the dark brown shale in the Grassy Creek, common in the argillaceous phase at the base of the Saverton, and scarce in the silty phase of the Saverton. Table I shows that the amount of chlorite is related directly to the amount of illite.

Muscovite:

The mineral identified as muscovite showed considerable resemblance to chlorite on the one hand and to illite on the other. The 2V of about 35^{0} and the indices of refraction for γ and β in (001) of about 1.60 are too high for illite. In 1.60 oil, muscovite virtually disappeared from view, while chlorite still stood out in

relief. Muscovite occurred in small rounded flakes, frequently with dark inclusions around the edge. A few grains showed undulose extinction. Krumbein and Pettijohn (1938, p. 462) listed the mineral as common and stable. The absence of correlation between the abundance of other micaceous minerals and of muscovite argues against authigenic origin. The dark material around the edge of the flakes probably was a degradation product. The evidence clearly favors detrital origin.

Pyrite:

Pyrite occurred as cubes, octahedrons, and small spherical concretions. The mineral appeared in greatest abundance in the clay at the base of the Grassy Creek and was common to abundant in the dark brown shale. Pettijohn (1949, p. 505) stated that pyrite commonly is associated with organic matter. The organic matter evidently furnished the sulfur as well as the reducing environment necessary to maintain iron in the ferrous state. That organic matter is not necessary to the formation of pyrite is indicated by the presence of some pyrite nodules in the silty phase of the Saverton shale. An abundance of excellently euhedral crystals of pyrite was noted locally in the arenaceous clay at the base of the Grassy Creek formation. The overlying thin bed of sandstone contains an abundance of marcasite. The presence of these iron sulfides is ascribed to leaching of iron and sulfur by descending solutions from the dark brown shale and

reprecipitation in more porous beds.

Goethite (limonite):

Four modes of occurrence of goethite were noted: 1. In very fine-grained, small, brown, spherical concretions. 2. In irregular fragments as an alteration product of pyrite. 3. As a yellow-brown stain on other minerals, principally quartz. 4. In small, tabular crystals, black metallic to brown-red in reflected light and intergrown with a white opaque mineral identified as leucoxene. The intergrowth of goethite and leucoxene was interpreted to be an alteration product of ilmenite. Goethite appears to be more prevalent in the Saverton than in the Grassy Creek formation. Table I indicates that the abundance of goethite is inversely proportional to the abundance of pyrite. This observation is in accord with the fact that the formation of pyrite requires reducing conditions, whereas the formation of goethite requires oxidizing conditions.

Leucoxene:

Leucoxene occurred as nearly opaque grains, white in reflected light. Most grains were associated with goethite in the manner described above. According to Milner (1940, p. 308) the mineral is derived from ilmenite. Leucoxene was slightly more abundant in the Saverton formation than in the Grassy Creek formation.

Rutile:

Rutile was one of the two most abundant constituents of the heavy mineral concentrate. Rutile occurred as small, irregular fragments with rounded edges and conspicuous striations in two directions. These fragments evidentally were of detrital origin. The mineral occurred also as fine needles, an occurrence which is clearly authigenic. One geniculate twin was found. Pettijohn (1949, pp. 504-505) suggested that rutile might form at the expense of leucoxene and ilmenite. Some rutile grains were noted which graded into leucoxene. Although rutile was equally common in both formations, the mineral seemed to be slightly more prevalent in the silty phase of the Saverton.

Zircon:

Two types of zircon were identified: very small prismatic grains with rounded edges, and large, nearly spherical, well frosted grains. The latter type was found not only in samples which contained abundant, large, round, frosted quartz grains but also in dark brown shale. Oriented overgrowths were not found, which indicates that the mineral is of detrital origin. Zircon is as abundant in the Grassy Creek as it is in the Saverton formation.

Tourmaline:

Tourmaline, like rutile, is one of the most abundant minerals in the heavy mineral concentrate. Grain size varied widely, but nearly all grains showed a perfectly

prismatic habit. Many grains were terminated by pyramid faces on at least one end and some on both ends. The shales contained larger euhedral grains of tourmaline than of any other mineral. Some grains were pleochroic from olive-green to pale yellow, others from blue to pale yellow. A few grains with color banding were noted. Pettijohn (1949, p. 504) pointed out that the lighter-colored secondary outgrowth is usually deposited at the negative end of the crystal in response to its hemimorphic habit. The wide variety in grain-size, the absence of abrasion, and the euhedral habit point to authigenic origin. The absence of color banding in most grains indicates that tourmaline did not form around a detrital core but crystallized directly.

Phosphate:

Phosphates were found in fossil fragments only, especially those of conodonts. The fragments were various shades of brown in transmitted light and black in reflected light. Birefringence was very low; most fragments showed rotary polarization. The index of refraction of 1.63 an the low birefringence correspond to the minerals dahlite, francolite, and fluor-apatite. Milner (1940, pp. 418-419) discussed phosphatic deposits and ascribed the dark color of phosphatic nodules to the presence of hydrocarbon.

Spectrographic Work

Semi-quantitative emission-spectrographic analyses of samples of raw shale were made by Dr. E. E. Pickett at the University of Missouri. Estimates of relative amounts of trace elements were made by visual comparison of line blackness, using a set of standards of known composition. It is believed that for the various samples the reported relative amounts of a given element are fairly accurate, but that the absolute amounts are considerably less accurate.

Table II presents the results of the spectrographic analyses. Figure 3 presents graphically average percentages of trace elements for each formation. Analyses of the Grassy Creek and Saverton formations exhibit considerable similarity, but the Saverton formation is poorer in Cu, Co, Mo, V, and Zn. This may be due to the higher percentage of clay minerals in the Grassy Creek formation, for clay minerals are capable of absorbing foreign ions. It may be due also to deposition of the Saverton beds in a more aggressive environment which leached out the more loosely bound trace elements.

TABLE II

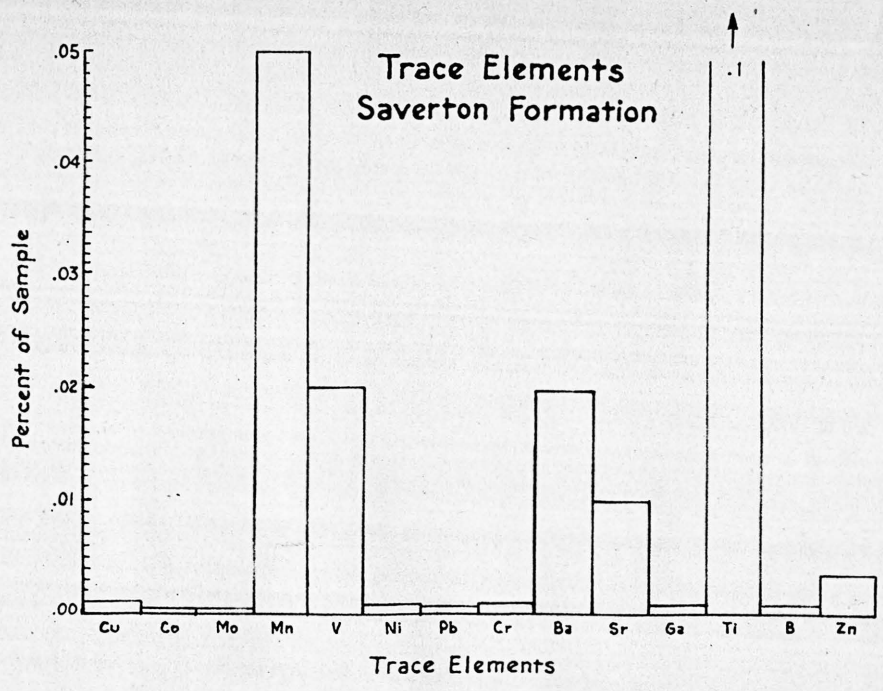
SPECTROGRAPH ANALYSIS FOR TRACE ELEMENTS IN THE GRASSY CREEK AND SAVERTON FORMATIONS OF MARION, RALLS, AND PIKE COUNTIES, MISSOURI

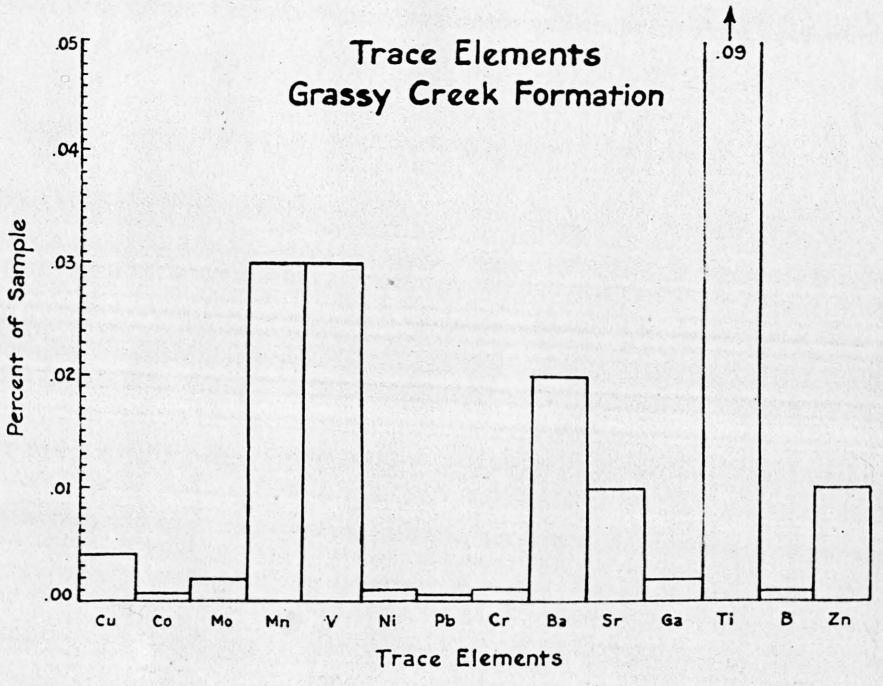
(performed by E. E. Pickett)

			Percent of Trace Elements													
Section Number	Sample Number	Formation	Cu	Co	Mo	Mn	V	Ni	Pb	Cr	Ba	Sr	Ga	Ti	B	Zn
I	8	Sav.	.001	.0003	.0003	.05	.01	.001	.001	.001	.02	.01	.001	.1	.001	-
I	6	Sav.	.0005	.0003	-	.05	.03	.001	.0003	.002	.02	.003	.001	.1	.001	.003
I	4	Gr. Cr.	.01	.003	.003	.02	.02	.002	.001	.001	.01	.005	.002	.1	.001	-
I	2	Gr. Cr.	.005	.001	.001	.01	.05	.001	.001	.001	.003	-	.002	.05	.001	.01
V	8	Sav.	.001	.0002	.0002	.05	.02	.001	.001	.001	.02	.01	.001	.1	.001	-
V	6	Sav.	.001	.0005	-	.02	.05	.001	.0005	.001	.01	.003	.001	.1	.001	-
V	5	Gr. Cr.	.001	.0003	.0005	.05	.02	.001	.0002	.001	.02	.005	.001	.1	.001	-
V	1	Gr. Cr.	.002	.0002	.005	.05	.02	.001	.0002	.001	.02	.005	.001	.1	.001	-
VI	5	Sav.	.0005	.0001	-	.05	.01	.0005	.0005	.001	.03	.03	.001	.1	.001	-
VI	3	Sav.	.0005	.0001	-	.05	.01	.0005	.0003	.001	.02	.01	.001	.1	.001	-
VII	6	Sav.	.001	.0002	.0005	.1	.01	.001	.001	.0005	.003	.005	.001	.05	.001	.005
VII	3	Gr. Cr.	.002	.0003	.002	.03	.05	.002	.0005	.001	.03	.03	.002	.1	.001	-
Average for Saverton			.0008	.0002	.0003	.05	.02	.0009	.0007	.001	.02	.01	.001	.1	.001	.004
Average for Grassy Creek			.004	.0006	.002	.03	.03	.001	.0006	.001	.02	.01	.002	.09	.001	.01

Trace elements which are absent: Ge, Li, Cd, Bi, Sb, Sn, Be, Ce, La, Ag.

Refer to Table I for location of the section, thickness of bed sampled, and lithologic description.





AVERAGES OF SPECTOGRAPHIC ANALYSES
FOR
TRACE ELEMENTS
IN THE
GRASSY CREEK AND SAVERTON FORMATIONS

Figure 3

Electron Micrographs

Electron micrographs of the size-fractions with particles below 10 microns in diameter were taken by Dr. J. H. Affleck at the University of Missouri. The magnification of these micrographs was 5000 diameters.

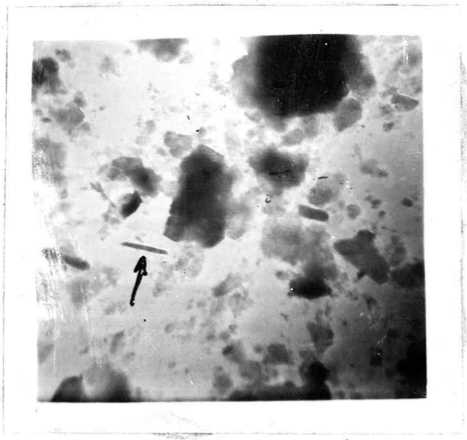
A significant feature of the micrographs was the presence of rod- or lath-shaped bodies, 1 to 4 microns in length, varing in width, and frequently exhibiting frayed or split ends. These rods were present in all samples and corresponded to descriptions of halloysite and nontronite by Davis, Rochow, et al. (1950, pp. 6-8 & p. 11).

The micrographs presented no definite evidence of illite or montmorillonite. Grim (1953, pp. 116-122) and Davis, Rochow, et al. (1950, pp. 8 & 11) pointed out that crystals of these minerals are notably lacking in distinctive features. Characteristic reflections on the X-ray spectrograms, however, placed the presence of illite beyond doubt.

Evidence for the presence of kaolinite was weak. A number of hexagonal flakes, corresponding vaguely to those described by Davis, Rochow, et al. (1950, p. 5) were detected. None of these flakes possesses the characteristic sharp outlines of kaolinite. The X-ray spectrograms, on the other hand, particularly those made of oriented clay mineral aggregates, exhibited the narrow

Saverton Formation - Section I, Interval 8.

2 micron



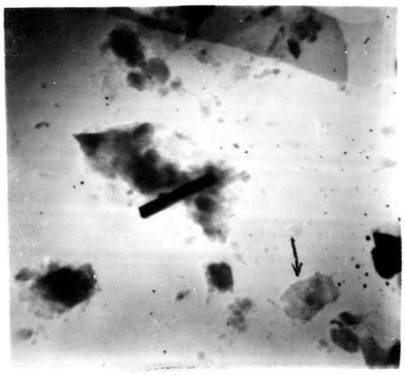
Grassy Creek Formation - Section V, Interval 1.

ELECTRON MICROGRAPHS SHOWING HALLOYSITE OR NONTRONITE

Figure 4

Saverton Formation - Section VI, Interval 5.

1 micron



Grassy Creek Formation - Section I, Interval 2

ELECTRON MICROGRAPHS SHOWING KAOLINITE

Figure 5

basal reflections characteristic of kaolinite. Halloysite should give considerably broader reflections.

Figures 4 and 5 show outlines of halloysite or nontronite and kaolinite crystals. It is believed that no conclusions can be drawn from the micrographs beyond the fact that either halloysite or nontronite is present in all samples. Considerably superior micrographs could be obtained by using a magnification of 20,000 and a size-fraction with particles below 1 micron in diameter.

SUMMARY OF RESULTS

Laboratory analysis indicates considerable analogy between the mineral assemblages of the Grassy Creek and the Saverton formations. The following discussion briefly considers some notable differences.

The Grassy Creek beds were found to contain predominantly quartz and illite in addition to lesser amounts of kaolinite, either halloysite or nontronite, chlorite, muscovite, feldspars, dolomite, pyrite, goethite, leucoxene, rutile, zircon, phosphate, and tourmaline. The Grassy Creek beds contain significantly more illite, chlorite, kaolinite, and pyrite than the Saverton beds.

The Saverton beds contain predominantly quartz, dolomite, and illite, in addition to lesser amounts of the other minerals already listed. The Saverton formation contains significantly more quartz, dolomite, calcite,

leucoxene, goethite, and rutile than the Grassy Creek formation and a significantly lower percentage of the trace elements Cu, Co, Mo, V, and Zn.

The facts presented lead to the preliminary conclusions that the Saverton beds were deposited in a more aggressive environment than the Grassy Creek beds, and also that the Saverton beds contain at least one component - dolomite - which could not have been derived in such abundance by erosion of the Grassy Creek beds.

The chapter which follows presents evidence which indicates that there was a gradual change from Grassy Creek to Saverton conditions of deposition, a change accompanied no doubt by some sub-aquous erosion of Grassy Creek beds, but not by removal of a major portion and subsequent redeposition as Saverton beds.

ENVIRONMENT OF DEPOSITION

MECHANICS OF DEPOSITION

The basal deposit of the Grassy Creek formation consists of an arenaceous clay shale, with abundant coarse, round, frosted quartz grains, phosphatic nodules, conodonts, and fish remains. Locally this basal shale contains small euhedra of pyrite. Rich (1951, p. 2025) interpreted similar material at the base of the Chattanooga shale as a lag-concentrate. Although round, frosted quartz grains are abundant locally at the base of the Grassy Creek formation and rare in the overlying dark brown shale facies, the basal deposit of the Grassy Creek formation does not exhibit these quartz grains everywhere, as is shown in Section III, Figure 2. The striking resemblance between the frosted quartz grains in the Grassy Creek formation and those in the St. Peter sandstone suggests a possible source area. It is unlikely that the frosted quartz grains were transported to the site of deposition by water, for the Grassy Creek formation consists predominantly of exceptionally well-sorted and very fine material. Rich (1951, p. 2027) suggested transportation by algae, which had lived along sandy beaches and had floated seaward, or by fishes, which had fed on marine organisms living on sandy coastal bottoms. A simpler explanation is that sand from coastal dunes blew seaward. The concentration

of sand grains above the unconformity can be explained as follows: A rising sealevel brought an end to planation and initiated a period of deposition of fine-grained argillaceous material. While deposition of this material was in progress, the wind, algae, or fishes brought in occasional course sand grains. In the initial deposit, the sand grains were well disseminated. A change of sealevel, a change of currents, or a temporary atmospheric disturbance of sealevel which lowered the wave base caused local reworking of the new deposit. Most of the fine particles were winnowed out, and the larger sand grains, phosphatic nodules, and fish remains were left. Winnowing destroyed the bedding and re-arranged the sand grains in irregular lenses.

Grains of coarse sand are absent or rare in thick deposits, such as the dark brown organic shale in Sections III and V, Figure 2, and exceedingly abundant in thin deposits such as the green clay shale in Section IV, Figure 2. Evidently, dark brown organic shale indicates undisturbed deposition, and green shale with abundant grains of sand indicates deposition alternated by reworking.

The basal deposit of clay shale is overlain by different material in different sections. This material varies from arenaceous shale and calcareous siltstone to very hard, well cemented sandstone. The arenaceous shale and the siltstone represent conditions of relatively undisturbed deposition. The sandstone consists of coarse,

round, frosted quartz grains cemented by secondary silica and represents either a considerable period of non-deposition of fine material or thorough winnowing out of previously deposited material.

The material described is overlain by dark brown organic shale, the environmental significance of which will be discussed in a separate section. Although in the sections examined the contact between the Grassy Creek and Saverton formations usually is sharp, the upper part of the dark Grassy Creek shale in some instances grades into lighter-colored, more arenaceous, and less thin-bedded material. Interval 5 of Section V, Figure 2, shows that the upper part of the Grassy Creek formation is no longer dark brown but dark gray. A similar condition can be observed in Interval 4 of Section VII in addition to small lenses of lighter-colored, more arenaceous shale within the darker shale. Interval 5 of Section III presents a more advanced stage : The Grassy Creek formation still contains organic matter, but it is now associated with siltstone. In Interval 6 of the same section organic matter is present only in small lenses of darker-colored shale within buff siltstone. Gradational effects were noted only in thick sections. Thin sections exhibited a sudden transition from dark brown organic Grassy Creek shale to blue-green Saverton shale. This indicates that toward the end of Grassy Creek time the water slowly became more ventilated in some localities, while in others,

presumably the topographic highs, the speed of currents increased sufficiently to remove some of the organic mud recently deposited. The fact that all sections present a sharp contact between the dark brown or gray Grassy Creek formation and the light gray to green Saverton formation indicates that some sub-aquous erosion or at least an interruption of deposition must have taken place everywhere.

Where the sedimentary section is thin, Saverton time was initiated by deposition of material nearly identical to that found at the base of the Grassy Creek formation. Once again, argillaceous material with disseminated, round, frosted quartz grains was deposited and winnowed out by currents to produce greater concentration of quartz grains. Where the sedimentary section is thick, deposition appears to have been more nearly continuous, several feet of fine clay shale having been deposited.

In late Saverton time the sediment gradually changed from primarily argillaceous to primarily arenaceous and dolomitic. This phenomenon can be variously interpreted: Uplift may have occurred in the source area, reducing chemical and enhancing mechanical erosion; a drop in sealevel may have lowered the baselevel of deposition; or the velocity of currents may have increased, causing a size-grade of material that was previously deposited nearer the source area to be carried out farther. Toward the end of Saverton time, sea water conditions became

favorable for chemical precipitation of calcite, which commenced to be deposited with the clastic material. The sudden transition from the calcareous siltstone of the Saverton to the lithographic limestone of the Louisiana formation indicates that most of the sediment which would have recorded the transition from clastic to chemical deposition was removed by sub-aquous erosion. When the erosion interval came to an end, sedimentation was resumed in the now clear sea with chemical deposition of Louisiana limestone.

DEPOSITION OF ORGANIC SHALE

General Considerations

Dark organic shales composed in part of visible plant materials which originally were cellulose or lignin are called humic shales. Shales composed in part of fatty, waxy, gummy, and resinous constituents are termed bituminous shales. Twenhofel (1939, p. 1186) pointed out that bacteria destroy organic matter in a bottom-mud in a definite sequence. This sequence starts with proteins, continues with starches and sugars, cellulose, lignin, and ends with fats, waxes, gums, and resins. The order of destruction suggests that formation of humic shale would require very poor circulation at the time of accumulation of the mud and that formation of bituminous shale would

require waters not completely stagnant. Limited circulation would lead to breaking down of only the first members of the sequence, which would allow organic matter to take on a more bituminous character. The Grassy Creek shale does not contain visible plant remains, and an oil can be produced from the shale upon destillation. The Grassy Creek shale therefore is classified as a bituminous shale.

The fauna of the bituminous shale is undoubtedly marine. The brachiopod fauna is very poor and is represented only by phosphatic shells of inarticulates such as Lingula, a hardy type, capable of survival under adverse conditions. No environmental significance can be attached as yet to the conodonts. The abundant fish remains suggest that the mud accumulated in water of sufficient depth to allow the existence of a well-aerated layer of water which could support fish life above the relatively stagnant bottom water. The fish remains could not have been washed in by currents, for these same currents would have made the formation of bituminous shale impossible.

Oxidation exceeds photo-synthesis in stagnant waters, and in time they are depleted of oxygen. Anaerobic bacteria partially decompose organic matter, liberating phosphates and sulphates. The sulphates are reduced to sulphides and hydrogen sulphide. The hydrogen sulphide, in turn, acts upon iron salts and precipitates black, amorphous iron sulphide, which recrystallizes later to

pyrite or marcasite. According to Strom (1939, p. 361) some recent stagnant bottom waters contained 40 cc H_2S per liter and 700 mg P_2O_5 per cubic meter. Some euxinic muds contained up to 23.4% organic carbon and 0.23% P_2O_5.

Krumbein and Schloss (1951, p. 374) pointed out that partial preservation of organic material can be accomplished, not only by poor circulation of oxygen-depleted waters, but also by rapid burial which removes organic material from the zone of decomposition at the surface of the mud. In this connection, it is of interest to remember that there is little change in fossil assemblage from the base of the Grassy Creek to the top of the Saverton formation, that wind-blown sand is especially sparsely disseminated through the dark organic shale as compared to the lighter-colored shale, and that pyrite is not much more abundant in the dark organic shale than in the lighter-colored shale. Rich (1951, p. 2022) believed that in the Tennessee-Alabama area, deposition of 20 feet of Chattanooga shale, a correlative of the Grassy Creek (s.l.) formation, took place from the beginning of the Late Devonian to well into the Early Mississippian. In spite of Rich's conclusion for the Chattanooga shale, the present writer believes that the dark shale of the Grassy Creek formation gives evidence in favor of rapid deposition.

Thin bedding and fissility are characteristic of many bituminous shales. Pettijohn (1949, p. 288) ascribed this to the colloidal nature of the original mud, which,

under removal of water, was compressed to perhaps one-fifth of its original thickness. Trask (1931, p. 275) pointed out that the initial water content of a sediment increases with decreasing particle size and increasing percentage of clay. The very fine-grained and argillaceous Grassy Creek mud may therefore have contained 80% water. Pettijohn (1949, p. 278) admitted the importance of recrystallization and parallel orientation of micaceous constituents at the time of deposition. The present writer noted a direct relation between fissility and content of illite. Illite and chlorite are formed authigenically out of other clay minerals. Fissility appears to be due, at least in part, to the orientation of authigenic illite and chlorite with their most prominent planes of cleavage parallel to the bedding. This orientation is caused, presumably, by initial deposition of particles parallel to the mud surface and subsequent growth perpendicular to the direction of greatest stress during compaction. Rich (1951, pp. 2024-2028) believed that fine laminations indicated quiet water without wave- or current-action, absence of scavengers, and absence of aquatic vegetation attached to the bottom, all of which would have destroyed the bedding.

Favorable Conditions

Strom (1939, pp. 361-364) described some conditions which favor formation of modern black organic muds.

Stagnation is favored by a warm climate, for at high temperature water exhibits greater density difference per degree increase in temperature from bottom to top than at low temperature. Greater density difference promotes more stable stratification and less convective overturn. Higher water temperatures promote quicker oxidation of organic matter and more rapid depletion of oxygen. Low tidal heights favor stagnation, for high tides promote thorough circulation and ventilation.

Suggested Environments

Moore (1933, p. 274) supposed that the Chattanooga shale was deposited by a sea which transgressed over a land area covered by black, humus-rich soils. It is by no means proved as yet that the Grassy Creek (s.l.) formation is time-transgressive. Mere reworking of a soil, futhermore, would not result in a wide-spread off-shore deposit of relatively thick and very well-laminated shale.

Twenhofel (1932, p. 815) remarked that organic shales may form in marine swamps. During times of low-lying lands, shallow epicontinental seas, and limited tidal ranges such swamps might have been tens or hundreds of

miles in width. Swamp deposits, however, are poor in marine fossils and commonly contain remains of higher plants.

Rich (1951, p. 2023) ruled out a lagoonal environment for the Chattanooga shale because of the lack of evidence of old sandbars which could have protected the lagoons from the sea.

Twenhofel (1939, pp. 1193-1194) suggested that bituminous shale might form in a shallow, nearly tideless, epicontinental sea. Circulation would be damped by aquatic plants such as kelp-like algae, and waves would break far off-shore. Storms would occasionally carry in plankton, nekton, and small benthos. With rising sealevel, the black mud belt would migrate with the shore, invading the land area and retreating on the seaward side. The Grassy Creek formation (s.l.) shows no evidence of interfingering between an euxinic and a ventilated environment such as would result from this suggestion. The sections examined gave evidence, rather, of a gradual and simultaneous change in conditions of deposition throughout a wide area. No aquatic plants were preserved in the shale, and there is no evidence of transgression.

Rich (1953, p. 1535) claimed that the Chattanooga shale was deposited in the fondo-environment - i.e., in quiet, unaerated water below wave base. Suggestions of fondo origin of the organic shale of the Grassy Creek formation are found in the fine-grained material, the

absence of cross or current-stratification, fine laminations, and abundance of light-weight organic matter. Strom (1939, p. 368) pointed out that the present tropical Atlantic Ocean contains only 1 cc. of oxygen per liter at a depth of 500 meters. The present ventilation is due to the connection of the Atlantic with the Arctic and Antarctic Oceans which supply cold subsurface oxygen-bearing waters. As Pettijohn (1949, p. 459) noted, the existence of polar ice-caps results at depth in an active equator-ward circulation of cold oxygen-bearing waters that have been ventilated near the surface. Were the ice-caps not present, circulation would stop, and the bottom waters of large areas of the present oceans would begin to stagnate. The Late Devonian climate was considerably warmer than that of the present day, and polar ice-caps were not present. Add to this the possibility that sub-marine barriers existed between polar and equatorial seas, and the probability exists that euxinic muds would accumulate in large areas of the seas. Indeed, organic shales were deposited during Late Devonian and Early Mississippian time in North America as well as Europe.

Trask (1932, p. 112) indicated phytoplankton as the source of the organic matter in modern marine sediments. The development of phytoplankton is governed by the available supply of nitrate and phosphate in the upper insolated layers of water. These nutrient materials can be derived from the land, from agitation of water and

bottom deposits in shallow environments, from decomposition of dead organisms in the surface layers of water, and from the upwelling of deeper water rich in nitrate and phosphate. Trask (1932, p. 240) found that modern near-shore sediments contain more organic matter than pelagic sediments. The present writer believes that with favorable prevailing winds and weak oceanic currents river waters with a rich supply of nutrients from the land could spread over a large part of the surface of the sea. This would insure uniform conditions for development of plankton over large areas, rather than just in the near-shore area.

Concluding Remarks

Review of the opinions of several writers and careful examination of the data provided by this study indicate that the bituminous shale facies of the Grassy Creek formation was formed below wave-base and by rapid deposition in an epicontinental sea with low tidal heights. Late Devonian and Early Mississippian climate was equable and warm, which implies little atmospheric disturbance, fairly shallow wave-base, and stable density stratification. Oceanic circulation was weak or absent. The surface layers supported an abundant population of phytoplankton and fish; the bottom could support only the hardier types of brachiopods.

DEPOSITION OF CLAY MINERALS

Review of General Occurrence and Formation

Allen (1937, p. 19) and Grim (1951, pp. 227-228) pointed out that illite is the dominant clay mineral in marine limestones and dolomites. Montmorillonite is the next most abundant clay mineral, particularly in the younger formations. Illite is the dominant clay mineral in all shales older than Mesozoic. Montmorillonite is usually absent in Paleozoic shales, although it does occur in abundance in Mesozoic sediments. Grim (1951, p. 229) suggested that illite forms from montmorillonite and possibly from kaolinite by a very slow diagenetic change. Illite is of marine origin, and according to Keller (1953b, p. 102) its formation is favored by water which is rarely renewed or freshened, by an alkaline pH, by abundant metal cations, and by the presence of potassium.

Grim (1951, pp. 226-228) pointed out that chlorite is present in nearly all Paleozoic shales, and that it is more abundant in ancient than in recent sediments, particularly in those of marine origin. Chlorite is believed to form authigenically from montmorillonite and possibly from kaolinite. Its formation is favored by a pH greater than 7 and by the presence of magnesium.

According to Grim (1951, pp. 227-228), kaolinite usually is absent in marine limestones and dolomites.

Allen (1937, p. 25) suggested that kaolinite and halloysite might form near the top of the weathered mantle of soil which has formed on a limestone or dolomite terrane - that is, in the thoroughly altered and leached zone. This suggestion corresponds to the opinion of Keller and Ting (1950, p. 130) and Grim (1951, p. 228) that the formation of kaolinite is favored by low pH, oxidizing environment, and active leaching which removes alkalies and alkaline earths as rapidly as they are liberated from the primary minerals. The presence of calcium impedes the formation of kaolinite. Grim (1951, p. 226) pointed out that kaolinite usually is absent in Paleozoic shales and is never abundant in these rocks. The mineral generally is absent in marine sediments, particularly the calcareous ones. Grim (1951, p. 230) believed that a kaolinitic marine sediment suggests a kaolinitic source area. Futhermore, the sediment would have to accumulate rapidly, or kaolinite could not persist in an environment fundamentally unfavorable to it.

Grim (1951, p. 230) quoted Hendricks, Ross, and Hadding as stating that glauconite is formed in the sea in a reducing environment maintained by bacterial action, an environment which probably remained unchanged for long periods of time. This implies that glauconite may form during times of decreased or negative sedimentation.

Occurrence in Sections Examined and Interpretation

The Grassy Creek and Saverton formations can be subdivided in four distinct environments of deposition.

The basal Grassy Creek sediment consists of arenaceous clay shale with abundant coarse, round, frosted quartz grains, phosphatic nodules, conodonts, and fish remains. This material is overlain by arenaceous shale, calcareous siltstone, or hard, well-cemented sandstone. These two types of sediment are poor in illite and chlorite and relatively rich in kaolinite. The low content of illite and chlorite attests to the fact that this depositional environment was well-ventilated. This corresponds to the concept presented above that the material is a reworked sediment, or, in Rich's words, a "lag-concentrate". The relative abundance of kaolinite is in agreement with the opinion that the formation and preservation of kaolinite requires an aggressive oxidizing environment but not at all with the idea that kaolinite is unstable in a marine environment. The possibility that the basal deposit emerged above sea-level and was leached should be entertained. It is difficult to visualize, however, how this deposit could have been leached on the land, whereas the immediately overlying deposit of only slightly younger age was deposited below wave base. It is believed that, in view of the presence of kaolinite throughout the section, even in sediments of undoubted marine and relatively deep water

origin, the concept of the instability of kaolinite in a marine environment may need qualification. The source area from which the basal Grassy Creek sediment was derived undoubtedly was rich in kaolinite; even reworking could not alter all kaolinite that was deposited.

The dark brown bituminous shale phase of the Grassy Creek formation is especially rich in illite and chlorite and contains an intermediate amount of kaolinite. The abundance of illite and chlorite indicates an environment of relatively stagnant water, alkaline pH, and abundant metal cations and potassium. This environment corresponds well with the site of deposition below wave base postulated previously. The intermediate amount of kaolinite points to rapid accumulation and burial of the sediment.

The basal Saverton sediment consists of fine clay shale containing disseminated, round, frosted quartz grains. This lithologic phase contains intermediate amounts of illite and chlorite and little kaolinite. The intermediate amounts of illite and chlorite are explained by the rising of the surface of deposition from the deeper euxinic environment into the shallower, better ventilated one. The smaller amount of kaolinite may attest to a decrease of kaolinite in the source area and also to slower accumulation and occasional winnowing of the sediment.

The upper Saverton sediment contains dolomitic and calcareous siltstone with little illite and chlorite and very little kaolinite. No montmorillonite was detected.

The low content of clay minerals is a result of the predominance of coarser clastic particles over finer ones. The well-aerated environment did not favor the formation of illite and chlorite. The coarser particles of quartz and dolomite indicate prevalent erosion of bedrock in the source area. This decreased the supply of kaolinite to an environment unfavorable to its preservation.

DEPOSITION OF NON-CLAY MINERALS

The mineral assemblages of the Grassy Creek and Saverton formations exhibit a few distinctive characteristics which can be interpreted in terms of a possible source area:

The greater abundance of dolomite, interpreted as of clastic origin, toward the upper part of the Saverton formation suggests erosion of dolomitic bedrock in the source area.

The greater abundance of calcite toward the top of the Saverton formation suggests a gradual change of conditions of sedimentation, a change which culminated ultimately in deposition of lithographic Louisiana limestone.

The presence of weathered-looking, roughly euhedral orthoclase grains suggests derivation from a limestone or dolomite terrane.

The larger percentage of leucoxene and rutile in the Saverton formation than in the Grassy Creek formation

reflects merely the greater transporting power of the waters of Saverton time.

PALEOGEOGRAPHY AND PROVENANCE

An attempt to determine the source area of the sediments of the Grassy Creek and Saverton formations takes into account the following factors:

1. The sediments were deposited rapidly. This is indicated by the persistence of kaolinite and the comparatively slight change from the fossil assemblage at the base of the Grassy Creek formation to that in the Louisiana limestone.

2. Possible land areas in the Late Devonian - Early Mississippian sea were the Central Kansas Uplift, the Kankakee Arch, and the Laurentian Shield. The Ozark Dome may have been a land area or may have been merely a shallow bank above wave base.

3. The Grassy Creek and Saverton formations become thicker toward the Illinois basin.

4. Krey (1924, p. 62) indicated that the Grassy Creek (s.l.) formation becomes more sandy toward the west.

Thickening to the northeast would imply that the source area was located in the northeast. On the other hand, the fact that the shales become more sandy toward the west would imply a westerly source area. The silt

and clastic carbonate in the upper part of the Saverton shale indicate, furthermore, that the source area could not have been very far off.

The data available at this time are too fragmentary to allow formulation of well-founded conclusions concerning the provenance of the Grassy Creek and Saverton formations. It is believed that study of these formations would have to be extended over a considerable larger area than the one involved in this report before a probable source area could be implied.

SUMMARY OF DEPOSITION

The ubiquitous presence of kaolinite throughout the sections examined suggests a possible dolomite - or limestone - terrane in the source area. This suggestion is substantiated further by the increasing abundance of clastic dolomite toward the upper part of the Saverton formation and the frequent presence of weathered euhedral grains of orthoclase. The present report does not cover an area of sufficient size to determine the provenance of the Grassy Creek and Saverton formations. Sufficient data are at hand, however, to reconstruct the local depositional history of these formations.

Sedimentation of the Grassy Creek formation was initiated by deposition of arenaceous clay shale. This sediment contained frosted quartz grains, blown in from

coastal dunes. A slight lowering of the wave base partially winnowed out the fine argillaceous material and resulted in a thin and non-bedded deposit of abundant frosted quartz grains with argillaceous material. According to present knowledge, kaolinite cannot persist in a marine environment unless it is buried rapidly; therefore, the abundant supply of kaolinite in this basal sediment suggests not only abundant supply of kaolinite from soils in the source area, but also a very brief period of winnowing. Sedimentation was resumed with deposition of arenaceous shale and siltstone. A thin local deposit of sandstone of eolian quartz grains suggests the immediate proximity of the wave base. A considerable subsequent rise in wave base allowed undisturbed deposition of bituminous shale in a poorly ventilated environment at the bottom of the sea, an environment overlain, however, by well-ventilated water that was capable of supporting a prolific growth of plankton. Low-lying land with a thick soil zone furnished abundant clay minerals and also plentiful organic material to support plankton development. The euxinic sedimentary environment favored the formation of abundant illite and chlorite. Rapid accumulation and burial of the sediment favored incomplete decomposition of organic matter derived from dead plankton as well as preservation of kaolinite. The formation of bituminous shale may have been promoted by a warm and equable climate, the absence of polar ice-caps, limited oceanic circulation, and low

tidal heights. The vertical gradation of dark bituminous shale into more arenaceous lighter-colored shale attests to the water slowly becoming more ventilated in some localities. On the topographic highs, currents removed some of the material already deposited. Deposition ceased eventually, and some sub-aquous erosion may have taken place throughout the area. Saverton time was initiated by a rise of wave base and deposition of fine clay shale. As indicated by the thinner sections with greater concentration of eolian quartz grains, some intermittent winnowing took place on the topographic highs. Intermediate amounts of illite and chlorite, a smaller amount of kaolinite than in the underlying bituminous shale of Grassy Creek time, and absence of bituminous matter all bear witness to the fact that the new environment was well-ventilated. The supply of kaolinite from the source area may have decreased due to erosion of progressively more bedrock rather than soil. Conditions of sedimentation favored next the deposition of argillaceous siltstone with considerable clastic dolomite as a result of more agitation of the water and, possibly, slight uplift in the source area. The greater velocity of the currents did not favor deposition of as abundant argillaceous material as before. Toward the end of Saverton time, conditions became favorable for chemical precipitation of calcite, which was deposited with the clastic material. A lowering of base level once again removed some material. When sedimentation

became possible once more, the supply of clastics had dwindled to such an extent that only lithographic Louisiana limestone could be deposited.

CONCLUSIONS

The mineralogical composition of the Grassy Creek and Saverton formations was determined by means of the X-ray-diffraction spectrometer and the petrographic microscope. Clay minerals identified were illite, kaolinite, halloysite or nontronite, chlorite, and muscovite. Non-clay minerals identified were quartz, orthoclase, microcline, plagioclase, calcite, dolomite, pyrite, goethite, leucoxene, rutile, zircon, phosphate, and tourmaline. No conclusions could be drawn from electron micrographs beyond the fact that either halloysite or nontronite were present in all samples in unknown amount. Spectrographic analysis indicated considerable similarity in trace mineral content between the Grassy Creek and Saverton formations.

A rough estimate was made of the relative abundance of each mineral in each sample. Both formations contained the same minerals. Quartz was the predominant mineral in either formation, though more abundant in the Saverton than in the Grassy Creek. Illite, chlorite, kaolinite, and pyrite were more abundant in the Grassy Creek, whereas dolomite, calcite, leucoxene, goethite, and rutile were more abundant in the Saverton formation. The Saverton formation contained a lower percentage of the trace elements Cu, Co, Mo, V, and Zn.

Four distinct environments of deposition were noted: The environment of early Grassy Creek time was well-venti-

lated and presents local evidence of winnowing. Late Saverton time witnessed stronger currents and deposition of a larger size-grade of material and a lesser amount of fine argillaceous material.

Complete gradation of the Grassy Creek into the Saverton formation was not encountered. Since abundant evidence for partial gradation was found, the diastem between the formations must represent only a relatively brief portion of time. It is not likely that a diastem of such small magnitude extends very far laterally. The stratigraphic literature indeed makes no mention of the occurrence outside the particular area of this study of a sharp contact between the Grassy Creek and Saverton formations.

Neither fish remains nor conodonts furnish evidence on which the Grassy Creek and Saverton formations could be differentiated.

The similar mineral assemblages, the closely related environments of deposition, the relatively small diastem between the formations, and the identical fossil assemblages are sufficient arguments against individual formational status for either the Grassy Creek or the Saverton beds. It is proposed, therefore, that the beds discussed in this report henceforth be designated as the Grassy Creek formation and that the dark brown shale facies be designated as the bituminous member of the Grassy Creek formation.

SUGGESTIONS FOR FURTHER WORK

Investigation of the mineralogy of the Grassy Creek formation offered a number of suggestions for further research. The suggestions listed below refer in part to future investigation of the Grassy Creek formation and in part to future investigation of shales in general.

1. Further light would be thrown on the problem of the source area by field study and detailed description of all surface exposures of the Grassy Creek formation throughout Missouri and adjacent Western Illinois.

2. Laboratory technique having been established, a few exposures of the Grassy Creek formation should be sampled at small intervals, and all samples should be analyzed.

3. A thorough paleontologic study should be made of a number of surface exposures to determine whether the Grassy Creek formation is or is not time-transgressive.

4. Mineral-grains identified as leucoxene should be segregated and studied by X-ray-diffraction to confirm this identification.

5. X-ray-diffraction spectrograms of standards should be used to estimate quantitatively the relative proportions of various clay minerals and quartz in spectrograms of raw shale samples.

6. Non-clay minerals should be determined quantitatively by weighing and grain count. A statistical study

of the effect on quantitative determinations of removal of all material below 10 microns in diameter would be of some interest.

7. Electron micrographs should be made of material below 1 micron in diameter. A magnification of 20,000 and the shadow-method of mounting the samples should be used. These micrographs would indicate whether the lath-shaped particles in samples from the Grassy Creek formation are halloysite or nontronite.

8. More detailed identification of clay minerals should be attempted by means of differential thermal analysis of clay-mineral concentrates.

9. Quantitative chemical analysis of a few samples of clay-mineral concentrate for Si, Al, Fe^{++}, Fe^{+++}, Mg, Ca, K, Na, Ti, and H_2O would greatly enhance the value of a mineralogical investigation of a shale.

10. Electron micrographs of peels of shale fragments would show the size, crystallinity, and arrangement of minerals in the shale. These peels should be obtained at various angles to the bedding.

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V I T A

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